Solvation processes in steam: *Ab initio* calculations of ion-solvent structures and clustering equilibria

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Reports of the high ion content of steam and low-density supercritical fluids date back to the work of Carlon [1], who invoked ion and neutral water clustering as as mechanism to explain why ions partition into the low-density aqueous phase. Mass spectrometric, vibrational spectroscopic measurements and quantum chemical calculations have refined this concept by proposing strongly bound ion-solvent aggregates and water clusters, e.g. Eigen and Zundel-type proton clusters $H_3O^+(H_2O)_m$ and the more weakly bound water oligomers $(H_2O)_m$. The extent to which these clusters affect fluid chemistry is determined by their abundance, however, little is known regarding the stability of such moieties in natural low-density high temperature fluids. Here we report, building on our recent report of the structures and energetics of protonated water clusters [2], results from quantum chemical calculations using high-accuracy multi-level G3 [2], and CBS-Q [4] theory to address this question. In particular, we have investigated the cluster structures and clustering equilibria for the ions $H_3O^+\cdot(H_2O)_m(H_2S)_n$, $NH_4^+\cdot(H_2O)_m(H_2S)_n$ and $H_3S^+\cdot(H_2O)_m(H_2S)_n$, where m≤6 and n≤4, at 300 to 1000K and 1bar as well as under vapour-liquid equilibrium conditions between 300 and 646K. We find that incremental hydration enthalpies and entropies derived from van´t Hoff analyses for the attachment of H_2O and H_2S onto H_3O^+, NH_4^+ and H_3S^+ are in excellent agreement with experimental values and that the addition of water to all three ions is energetically more favourable than solvation by H_2S. As clusters grow in size, the energetic trends of cluster hydration begin to reflect those for bulk H_2O liquids, i.e. calculated hydration enthalpies and entropies approach values characteristic of the condensation of bulk water (ΔH=-44.0 kJ·mol^{-1}, ΔS=-118.8 J·K·mol^{-1}). Water and hydrogen sulphide cluster calculations at higher temperatures indicate that a significant fraction of H_3O^+, NH_4^+ and H_3S^+ ions exists as solvated moieties.

References

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Constraints on the Earth's mantle heat budget from mantle plumes

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Mantle plumes may be derived from thermal boundary instabilities in the bottom thermal boundary layer (e.g., the core-mantle boundary) of the convective mantle and may contain important information on the heat transfer across the bottom thermal boundary layer. Plume heat flux and plume excess temperature in the upper mantle have been constrained by a variety of surface observations. A recent study on plume dynamics in 3-D regional spherical models by Zhong (2006) showed that these inferred plume heat flux and plume excess temperature for the upper mantle can be used to constrain the heat flux from the core to be ~35%-40% of the total surface convective heat flux and internal heating rate for the mantle to be ~60%-65%, depending on whether mantle convection is layered or whole-mantle convection. Here, we extended this study by computing models for a large parameter space (particularly different mantle rheology) and a much improved resolution and also by considering different criteria for detecting plumes. The new results confirmed that ~30-35% of the surface convective heat flux or ~10-12 TW needs to be derived from the core. We demonstrated that plume heat flux may account for ~90% of the core heat flux when plumes are generated above the CMB but plume heat flux decreases significantly as plumes ascend from the lower mantle to the upper mantle by a factor of ~2. More importantly, we demonstrated that the reduction of plume heat flux as plumes ascend is mainly caused by the large adiabatic cooling of plumes due to their excess temperature, while subadiabatic temperature only contributes less than 30% towards the plume heat flux reduction. We also showed that the plume temperature follows the adiabat for the plumes, and this provides a new approach to constrain the CMB temperature or the averaged dissipation number for the mantle from plume temperature in the upper mantle. Our results again suggest that for cooling rates less than 70K/Ga, the radiogenic heat generation rate for the MORB source regions needs to be more than 4 times higher than that for the depleted mantle.